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EFFECT OF COMPOSITION ON Bi_2O_3–SiO_2–GeO_2 GLASS PROPERTIES

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Glasses with composition $Bi_4(Si_xGe_{1-x})_3O_{12}$, where $x = 0.33$, 0.5 and 0.06, were obtained by melting for 30 min and two-step melting. Their characteristic temperatures, densities, refractive indices and microhardness were determined and the composition dependences studied.

Key words: bismuth-containing glass, characteristic temperatures, density, refractive index, microhardness.

Glasses in the system Bi_2O_3–GeO_2–SiO_2 are used in optics, electronics, and the telecommunications industry as laser materials when doped with rare-earth elements and as cryogenic charged-particle detectors when reduced in a hydrogen atmosphere.

The possibility using these glasses as a basis to obtain glass ceramic materials with scintillation properties is of greatest interest, since many sensitive scintillation elements currently used have a number of substantial drawbacks. For example, NaI and LiI crystals are hygroscopic, which causes instruments to malfunction; CsI is nonhygroscopic but it is unstable under high irradiation doses, which sharply curtails its applicability. ZnS single crystals cannot be used to detect γ-radiation because of the lose transmission in the visible range. The range of application of single-crystal KI is limited by the presence of ^{40}K in it. In addition, each material mentioned above requires activating additives, which are required in order for it to scintillate.

In this light there is promise in using single crystals with the structure of eulytin ($Bi_4X_3O_{12}$, where X = Si, Ge) as the active element, since the centers of emission are bismuth ions, making activators unnecessary. For equal volumes BGO and BSO crystals show higher photon detection efficiency than other scintillation crystals. The undoubted advantages of eulytins are their mechanical properties and nonhygroscopicity.

In view of the difficulties arising in growing eulytin crystals, which greatly increase production costs, a step forward is the use of glass ceramic materials based on glasses with equivalent composition. Matrix glasses are produced using well-perfected classic technologies, and glass ceramic materials can be obtained from them by easily accessible methods — heat treatment or laser irradiation.

Transparent glass ceramic materials based on glass with the compositions $2Bi_2O_3$;$3SiO_2$ and $2Bi_2O_3$;$3GeO_2$, containing up to 70% eulytin crystallites and possessing scintillation properties close to those single crystals, have now been obtained. As in the case of single crystals these properties of bismuth-germanate glass ceramics are higher while the radiation resistance is lower than for bismuth-silicate. In turn, bismuth-silicate glass ceramic is characterized by the opposite properties (the scintillation properties are lower but the radiation resistance is higher) [1]. Therefore, combining the useful properties of both materials in a single material is a topical problem.

Most works are devoted to studying phase equilibria in the binary systems Bi_2O_3–GeO_2 and Bi_2O_3–SiO_2. The ternary system Bi_2O_3–GeO_2–SiO_2 has been less studied. Glass formation in the indicated system was studied in [2]: the characteristic temperatures were determined, nontransparent glass ceramic materials based on these glasses were obtained, and the composition of the crystallizing phases and the lattice parameters of the crystals formed were determined.

The authors of [3] obtained samples of glasses with different ratios of Bi_2O_3, GeO_2 and SiO_2, in which the molar fraction of each glass-forming oxide (GeO_2, SiO_2) varied from 0 to 100%. On the basis of their results the authors conclude that solid solutions can form for any ratios of these oxides.

In the basis of these results it can be supposed that material possessing quite high radiation resistance and good scintillation properties at the same time can be obtained by varying the ratio of the silicon and germanium oxides in the system Bi_2O_3–GeO_2–SiO_2.

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The objective of the present work was to obtain glasses with the compositions $Bi_4(Si_xGe_{1-x})_3O_{12}$, where $x = 0.33$, 0.5 and 0.66, and to study the composition dependence of a number of their physical-chemical properties.

The composition of the initial batch was calculated on the basis of the ratio of the components of $Bi_4(Si_xGe_{1-x})_3O_{12}$, where $x = 0.33$, 0.5 and 0.66 (molar ratios $SiO_2:GeO_2$ = 1:2, 1:1 and 2:1, respectively).

A mixture of the powders was placed into a corundum crucible and sintered for 10 h in a muffle furnace at 750°C, grinding the crust periodically. The batch was pre-synthesized in order to decrease the homogenization time of the molten glass.

The batch obtained was melted in platinum crucibles at 1100°C in a resistance furnace without mechanical mixing of the melt. The glasses were poured onto a steel substrate pre-cooled to –18°C to keep them from crystallizing.

Experiments with different melting times of the initial batch (30 min, 2 h) were performed in order to optimize the glassmaking regime. Visually transparent glass samples with molar ratios $GeO_2:SiO_2$ = 1:1, 1:2 and 2:1 and red-brown color of different intensity were obtained. The samples obtained by melting for 30 min had a lighter color but a large number of nonuniformities because the homogenization time was too short. These defects had a negative impact on the stability of the glass during mechanical working and optical measurements. The samples obtained by melting for 2 h contained virtually no visible nonuniformities but their color changed to dark-brown.

Glasses with the indicated compositions with no or only a small number of defects and a lighter color were obtained by the procedure proposed in [4] — two-step melting: melting for 2 h followed by repeat melting for 30 min.

A so-called amorphous halo with no sharp peaks is present in the x-ray diffraction patterns of all samples, which shows that the materials obtained are glass with no inclusions of a crystalline phase.

The method used to form the glasses made it possible to obtain samples with prescribed geometric parameters, such as rods and plates, for subsequent dilatometric analysis and measurement of the density. The glass samples were ground and mechanically polished for subsequent studies.

The characteristic temperatures — glass-forming temperature t_g, dilatometric softening temperature t_s and the annealing temperature t_a required to remove the thermal stresses — were determined from the curves obtained (Fig. 1). The data are recorded in Table 1. For comparison

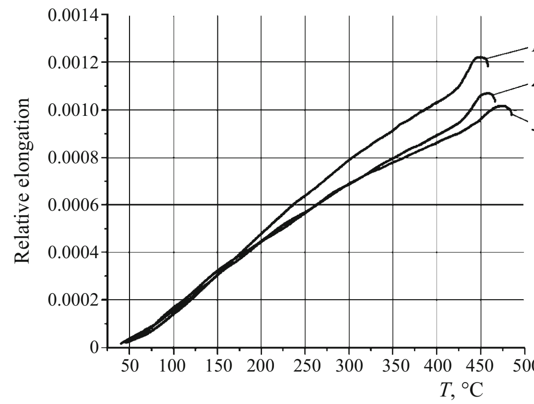

Fig. 1. Temperature dependence of the relative elongation of the samples obtained by two-step melting: *1*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$; *2*) $Bi_4(Si_{0.5}Ge_{0.5})_3O_{12}$; *3*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$.

the results obtained in [2] by differential-scanning calorimetry are also presented in the table.

As the content of silicon oxide increases the characteristic temperatures of the experimental glasses increase, since silicon oxide is more refractory. The energy of the Ge–O bond (355 kJ/mole) is less than that of the Si–O bond (465 kJ/mole). The decrease of the characteristic temperatures with increasing concentration of silicon oxide could likewise be due to the isomorphic substitution of Si for Ge atoms, as a result of which the structural motif of the glass becomes less ordered, as a result of which it becomes less thermally stable.

The glass-forming temperature of all samples is close to the values t_g obtained in [2] for the same compositions. The difference in their values is due to the fact that the dilatometric determination of the characteristic temperatures was made using samples in the form of rods while the data obtained with DSC are valid for dispersed glass.

To remove thermal stresses the glasses were annealed over 3 h in a muffle furnace at temperatures based on dilatometric studies, after which they were allowed to cool slowly. The stresses in the glasses could not be evaluated using a polariscope because of the dark color of the samples. For this reason the stresses in the samples were determined indirectly, according to the resistance of the samples to mechanical working (grinding and polishing).

To determine the density of the samples rods were fabricated in the form of rectangular parallelepipeds for conve-

TABLE 1.

Sample No.	Composition	Molar ratio $SiO_2:GeO_2$	t_a, °C	t_g, °C	t_g, °C (according to the data in [2])	t_s, °C
1	$Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$	1:2	310	422	435	452
2	$Bi_4(Si_{0.5}Ge_{0.5})_3O_{12}$	1:1	330	429	436	462
3	$Bi_4(Si_{0.66}Ge_{0.33})_3O_{12}$	2:1	348	437	438	481

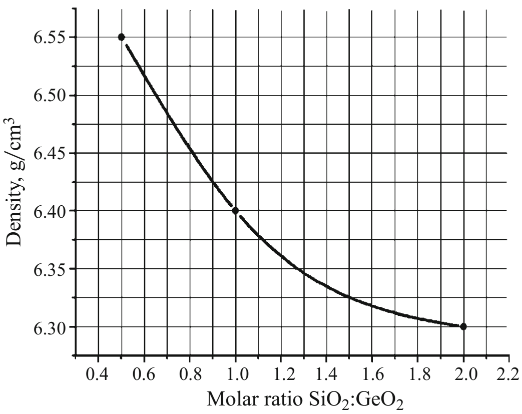

Fig. 2. Density of $Bi_4(Si_xGe_{1-x})_3O_{12}$ glasses obtained by two-step melting versus the composition.

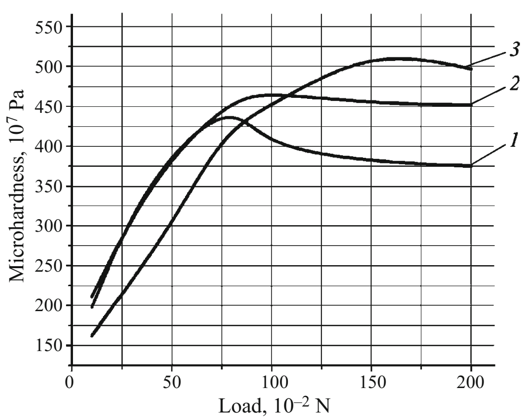

Fig. 3. Microhardness versus the load for samples obtained by melting for 30 min: *1*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$; *2*) $Bi_4(Si_{0.5}Ge_{0.5})_3O_{12}$; *3*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$.

nient and accurate calculations of the volume). The density was calculated from the relation

$$\rho = \frac{m}{V}.$$

The computational results obtained using the density measurements are presented in Fig. 2 in the form of curves of the density versus the ratio of the glass-forming oxides in the initial batch.

As is evident from the plot the density of the samples increases with the germanium oxide content. The density increase could be due to several factors. In the first place, if silicon oxide is conventionally taken to be the main glass former, an isomorphic substitution of Ge for Si can occur when germanium oxide is added to it. As a result of the difference of their atomic masses the density of the glass increases. In the second place, each glass-forming oxide can form its own polyhedra, comprising two independent networks and resulting in a lower average molar volume, higher density, and

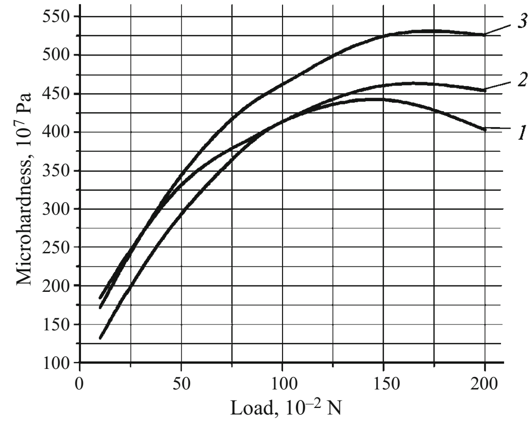

Fig. 4. Microhardness versus the load for samples obtained by two-step melting: *1*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$; *2*) $Bi_4(Si_{0.5}Ge_{0.5})_3O_{12}$; *3*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$.

lower glass-formation temperature. This correlates with the data of [2], which were obtained on the basis of experiments on diffusion through glass samples. The structure of the glassy germanium oxide is more compact compared with silicon oxide, since the valence angle Ge–O–Ge is smaller than the Si–O–Si angle, so that the free volume of the glassy germanium oxide is somewhat smaller than that of silicon oxide in the glassy state, and therefore the density is higher.

The refractive index of samples obtained by two-step melting was determined by Lodochnikov's method. The results are presented in Table 2.

The refractive index is higher in samples containing more GeO_2. This agrees with their density values.

The microhardness was determined by the Vickers method. A regular tetrahedral pyramid with vertex angle 136° was used as the indentor. The microhardness H_μ was calculated using the relation $H_\mu = 1.854 \times 10^5 F/d^2$, where F is the load and d is the diagonal of the imprint.

The microhardness measurements were performed under loads 0.5 – 2 N. Plots of the microhardness versus the load were constructed from the measurement data (Figs. 3 and 4) and the average microhardness values were calculated (Table 3). To confirm the influence of the glassmaking regime on the glass quality (specifically, on the mechanical characteristics of the glass) the microhardness values for samples obtained by two-step melting and melting for 30 min are presented on the plots. The measurements were performed after the samples were annealed in order to remove the thermal stresses.

TABLE 2.

Sample composition	Molar ratio SiO_2:GeO_2	Refractive index (±0.02)
$Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$	1:2	2.2
$Bi_4(Si_{0.5}Ge_{0.5})_3O_{12}$	1:1	1.9
$Bi_4(Si_{0.66}Ge_{0.33})_3O_{12}$	2:1	1.8

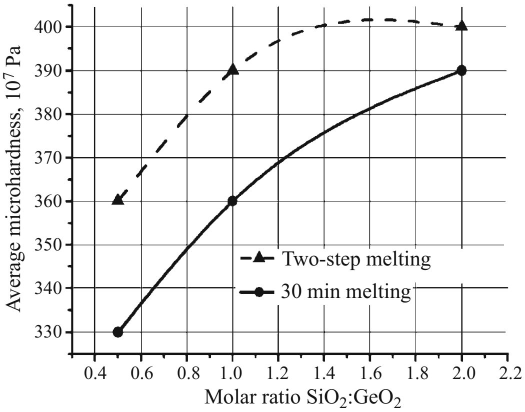

Fig. 5. Average microhardness versus the molar ratio of glass-forming oxides in different melting regimes: *1*) two-step melting; *2*) melting for 30 min.

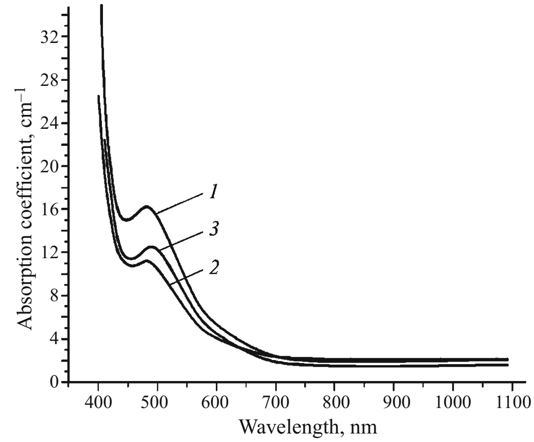

Fig. 6. Absorption spectra of glasses with the compositions: *1*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$; *2*) $Bi_4(Si_{0.5}Ge_{0.5})_3O_{12}$; *3*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$, fabricated by melting for 30 min.

For samples with the compositions $Bi_4(Si_{0.5}Ge_{0.5})_3O_{12}$ and $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$ the yield stress shifts to larger loads, since as the melting time increases the homogenization improves, the glass composition is smoothed, the glass network undergoes ordering and becomes denser, warning of the possibility defects being formed.

The microhardness of the samples with composition $Bi_4(Si_{0.66}Ge_{0.33})_3O_{12}$ (No. 3) is higher than for the other samples under all loads. The hardness is a function of the bond strengths and packing density of the atoms in the structure, while the energy of the Ge–O bond (355 kJ/mole) is less than that of the SiO bond (465 kJ/mole), so that the samples containing the maximum amount of silicon oxide are more stable against mechanical action.

The data on the average microhardness of the samples are presented in Table 3 and Fig. 5.

The absorption spectra of the glass samples with the compositions $Bi_4(Si_xGe_{1-x})_3O_{12}$, where $x = 0.33$, 0.5 and 0.66, fabricated by melting for 30 min and by two-step melting were obtained on a UNICO 2800 (UV/VIS) spectrophotometer with measurement range 190 – 1100 nm. The results of the spectral analysis for the glasses are presented in Figs. 6 and 7.

The samples in each series possess high transmission, irrespective of composition, in the UV range starting at 700 nm. The short-wave absorption edge lies near 400 nm. Absorption peaks whose nature is not fully understood are present near 500 nm. All authors [4, 5] attribute them to the presence of bismuth centers but there is no unanimous opinion about their nature (ions Bi^+, Bi^{2+}, Bi^{5+}; dimers Bi_2, Bi_2^- and Bi_2^{2-}). For samples of all compositions obtained by two-step melting the intensity of the peaks at 500 nm is lower than for samples obtained by 30-min melting. This explains the color difference for glass obtained using different melting regimes.

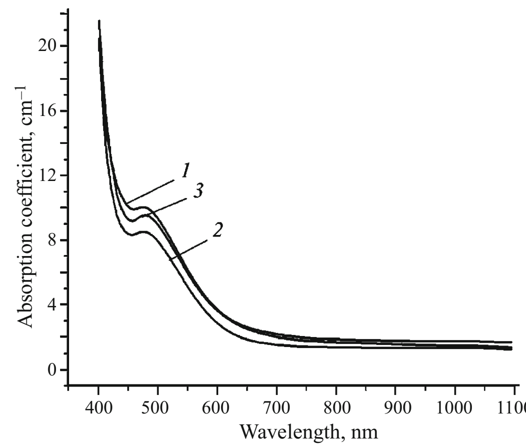

Fig. 7. Absorption spectra of glasses with the compositions: *1*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$; *2*) $Bi_4(Si_{0.5}Ge_{0.5})_3O_{12}$; *3*) $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$, fabricated by two-step melting.

TABLE 3.

Sample composition	Molar ratio SiO_2:GeO_2	Average microhardness, 10^7 Pa	
		Two-step melting	30 min
$Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$	1:2	360	330
$Bi_4(Si_{0.5}Ge_{0.5})_3O_{12}$	1:1	390	360
$Bi_4(Si_{0.66}Ge_{0.33})_3O_{12}$	2:1	400	390

The spectral characteristics of samples obtained by two-step melting are close. The small differences between the intensities of the peaks at 500 nm could be due to composition nonuniformities.

Samples of glasses in the system Bi_2O_3–SiO_2–GeO_2 with glass-forming oxides ratios (GeO_2:SiO_2) = 1:1, 1:2 and 2:1 were obtained by 30-min melting as well as two-step melting (2 h followed by re-melting for 30 min for fining).

As the germanium oxide content in the glasses increases the density and refractive index of the samples increase while the microhardness and characteristic temperature decrease. This is due to the difference of the atomic masses, the valence angles and energies of bonds with Si and Ge atoms, which form isomorphic solid solutions.

For glass samples with all compositions, distinct peaks due to the presence of bismuth centers are observed in the absorption spectra near 500 nm. When the two-step melting regime is used the glass samples become lighter in color and the observed peaks become weaker.

The optimal regime for preparing glasses with a prescribed composition is two-step melting. Because of better homogenization of the melt the samples obtained in this manner contain less nonuniformity and their color is lighter due to the low absorption coefficient at wavelength 500 nm and the microhardness is higher.

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